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# Enhanced nonlinear absorption and optical limiting in semiconducting polymer/methanofullerene charge transfer films

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Nonlinear optical absorption in solid films of poly(3-octylthiophene) (P3OT) sensitized with methanofullerene was investigated for wavelengths from 620 to 960 nm. The nonlinear absorption is enhanced over that in either of the component materials by more than two orders of magnitude at 760 nm. The large nonlinearity results from efficient photoinduced intermolecular charge transfer from P3OT to methanofullerene, followed by absorption in the charge separated excited state. P3OT/fullerene films are promising as optical limiters; the transmission clamps at an average fluence of approximately 0.1 J/cm<sup>2</sup>. The damage threshold was 15  $\mu$ J/pulse ( $\approx$ 1 J/cm<sup>2</sup> in average fluence), above which there is a permanent change in the linear transmission. © 1995 American Institute of Physics.

When C<sub>60</sub> or C<sub>60</sub> derivatives are mixed with a semiconducting polymer, the composite shows efficient photoinduced charge transfer.<sup>1–5</sup> Charge transfer and charge separation (with electron on the C<sub>60</sub> and hole on the conducting polymer) were demonstrated by photoinduced electron spin resonance, which exhibits *g* value labeled signatures of both the semiconducting polymer cation and the C<sub>60</sub> anion.<sup>1</sup> Spectroscopic signatures of the C<sub>60</sub> anion have been observed in photoinduced absorption (PIA) measurements.<sup>2</sup> Subpicosecond time-resolved PIA data show that charge transfer occurs within 300 fs after photoexcitation.<sup>4,5</sup> Since the charge transfer rate is more than 1000 times faster than any competing process, the quantum efficiency for charge separation approaches unity.<sup>1–8</sup>

In this letter, we summarize the nonlinear optical (NLO) absorption of P3OT/fullerene derivatives in solid films using nanosecond laser pulses at wavelengths from 620 to 960 nm (1.3–2.0 eV). We find a large nonlinearity, enhanced over that in either of the component materials by more than two orders of magnitude at 760 nm, which results from efficient photoinduced intermolecular charge transfer followed by absorption in the charge separated excited state. The NLO absorption of P3OT/methanofullerene blends is sufficiently large that photoinduced charge transfer films are promising as optical limiters (optical surge protectors). When pumped at 760 nm, the transmitted energy saturates at an average fluence of approximately 0.1 J/cm<sup>2</sup>.

The molecular structure of the soluble fullerene derivatives,<sup>9</sup> denoted as (6,6) PCBCR (phenyl-C<sub>61</sub>-butyric acid cholesteryl ester; MW=1164) is shown in Fig. 1. With these soluble C<sub>60</sub> derivatives, one can make homogeneous, stable, optical quality films containing 1:1 by weight methanofullerenes (approximately one acceptor for every five repeat units of P3OT).

For comparative studies, solid films were made of pure (6,6)PCBCR, pure P3OT, and a 1:1 (by weight) mixture. Each material was dissolved in xylene. Thick films (20–30  $\mu$ m) for NLO absorption experiments at off-resonant wavelengths were cast from filtered solution onto fused silica substrates. Thin films (0.1–0.2  $\mu$ m thick) for measurements near resonance and for third harmonic generation (THG) experiments were prepared by spin coating. All samples were kept in vacuum ( $\sim 10^{-6}$  Torr) during experiments to minimize photo-oxidation.

Transmission (*T*) and NLO absorption were measured for wavelengths from 620 to 960 nm using a pulsed dye laser pumped by the second harmonic of a *Q*-switched Nd:YAG laser. The full width at half-maximum of the dye laser pulse was 8 ns with a repetition rate of 10 Hz. At each wavelength, the dye laser beam was loosely focused, and the sample was translated along the optical axis (*z* axis) through the focus. The Gaussian beam radius at focus (radius at 1/*e* of the maximum electric field) was estimated to be  $\sim 25$   $\mu$ m. To obtain the nonlinear change in transmission ( $\Delta T/T$  versus *Z*), all the transmitted light was collected by a lens onto a silicon photodiode (open aperture *Z* scan).<sup>10</sup> Closed aperture *Z* scans were also tried; however, nonlinear refraction could not be observed because the nonlinear absorption was dominant.

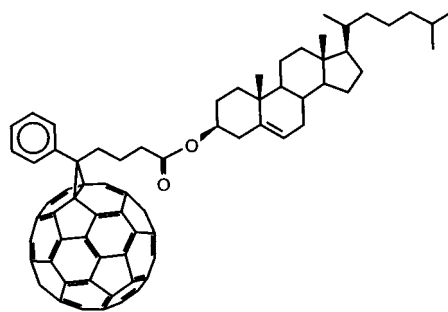


FIG. 1. Chemical Structure of (6,6)PCBCR (phenyl-C<sub>61</sub>-butyric acid cholesteryl ester).

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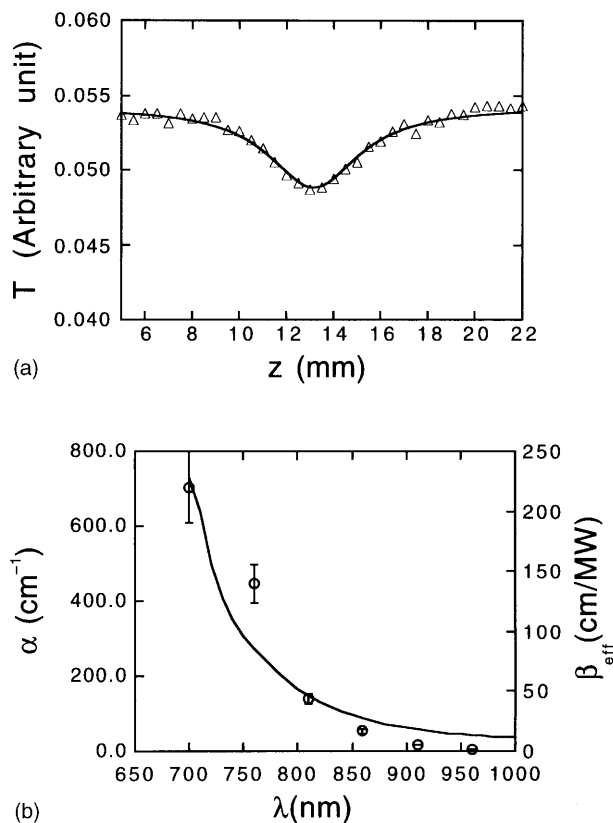


FIG. 2. (a) Open aperture Z-scan data and fit with  $\beta_{\text{eff}} = 140$  cm/MW (wavelength, 760 nm, input energy,  $0.2 \mu\text{J}/\text{pulse}$ ; and film thickness,  $30 \mu\text{m}$ ). (b) Dispersion of  $\beta_{\text{eff}}$  (open circles; right vertical axis) compared with the linear absorption spectrum of a thick film of the composite (solid curve; left vertical axis).

Typical Z-scan data are shown in Fig. 2(a) with the best fit to a model based on pure two-photon absorption (TPA) assuming Gaussian spatial and temporal laser intensity profiles.<sup>10</sup> The “effective” TPA coefficient  $\beta_{\text{eff}}$  provides a good description of the nonlinear absorption coefficient  $\Delta\alpha(I) = \beta_{\text{eff}}I$ , where  $I$  is the intensity. The  $\beta_{\text{eff}}$  values obtained from the fits are summarized in Table I. We found that  $\beta_{\text{eff}}$  is weakly dependent on the input optical pulse energy, decreasing slightly at higher input pulse energies; the  $\beta_{\text{eff}}$  in Table I as obtained in the low input energy regime ( $\Delta T/T < 0.2$ ), where the values are constant within the experimental error. At 760 nm, the NLO absorption is enhanced by more than two orders of magnitude in the composite film over that in the films of pure P3OT for pure (6,6)PCBCR. This is indeed nonlinear absorption; thermal effects (which might be significant for Z-scan measurements in the nanosecond regime) are ruled out by the large enhancement from the blend

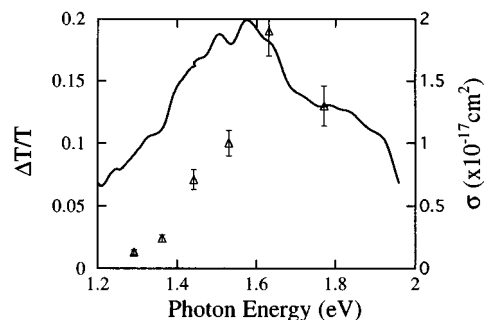


FIG. 3. The dispersion of excited state absorption cross section ( $\sigma$ ) is compared with the picosecond PIA spectrum (see Ref. 5).

over the pure P3OT and pure (6,6)PCBCR films. Since the three films have nearly the same optical density at the wavelengths, where the measurements were carried out, heating would be the same for the blend and for the pure film.

In Fig. 2(b), the spectral dependence of  $\beta_{\text{eff}}$  for the composite film is compared with the linear absorption coefficient  $\alpha$  of the same thick film. The relative experimental error at each wavelength was determined either by the minimum resolvable  $\Delta T/T$  or by averaging several data sets with different input energy per pulse, whichever is larger. An absolute error of  $\sim 20\%$  is expected from a combination of the errors in pulse energy and film thickness measurements, and from deviations from Gaussian pulse profiles. The spectral dependence of  $\beta_{\text{eff}}$  follows the absorption coefficient which decreases with increasing wavelength (in the tail of the  $\pi$ - $\pi^*$  absorption). We observed nonlinear bleaching at 620 nm (Table I). This arises from the shift in oscillator strength from the interband transition characteristic of the ground state to the absorption from the charge transferred excited state.<sup>4-6</sup>

The NLO absorption does not arise from a Kerr-type  $\chi^{(3)}$  process. The values for  $\beta_{\text{eff}}$  are too large ( $\sim 10^4$  times) compared with typical TPA coefficients obtained from similar organic systems with physically reasonable oscillator strengths.<sup>11,12</sup> Moreover, THG measurements of P3OT and of the P3OT/(6,6)PCBCR composite show no enhancement of any two-photon resonance.

We propose that the nonlinear absorption arises from photoinduced charge transfer followed by absorption from the charge transferred excited state. Although 760 nm is below the principal  $\pi$ - $\pi^*$  absorption, there exists a small residual absorption coefficient ( $\sim 270 \text{ cm}^{-1}$ ), mainly from the P3OT component, which is large enough to initiate the process. We have reanalyzed the Z-scan data using this model. The rate equation for the excited state population can be written as follows:

TABLE I. Effective two photon absorption coefficients  $\beta_{\text{eff}}$  (cm/MW) of the three films.

$\lambda(\text{nm})$	620	700	760	810	860	910	960
P3OT	a	$5.6 \pm 1$	$0.76 \pm 0.1$	$1.3 \pm 0.1$	$0.8 \pm 0.2$	$0.6 \pm 0.3$	$< 0.3$
PCBCR	No data	$< 60^b$	$0.6 \pm 0.1$	$0.3 \pm 0.2$	$< 0.2$	$< 0.3$	$< 0.3$
Composite	a	$220 \pm 30$	$140 \pm 16$	$44 \pm 4$	$17 \pm 2$	$5.3 \pm 0.5$	$1.6 \pm 0.2$

<sup>a</sup>Negative value (bleaching)

<sup>b</sup>Intensity-dependent.

$$dN/dt = \alpha I / \hbar \omega - N / \tau, \quad (1)$$

where  $N = N(r, z, t)$  is the number density of charge separated excited states generated by linear absorption with absorption coefficient  $\alpha$ ,  $I = I(r, z, t)$  is the intensity of the laser pulse at time  $t$  and coordinate  $(r, z)$  inside the medium,  $\hbar \omega$  is the photon energy, and  $\tau$  is the decay time of the charge separated excited state. The last term can be neglected since the decay time is much longer than the optical pulse width. To calculate the nonlinear energy transmission, the propagation equation

$$dI/dz = -\alpha I - \sigma NI \quad (2)$$

was numerically solved simultaneously with Eq. (1), where  $\sigma$  is the cross section for absorption from the charge separated excited state to a higher lying state. The second term produces nonlinear fluence-dependent loss due to the integration of  $I(z)$  in Eq. (1) with time.

Fitting the nonlinear absorption data to Eqs. (1) and (2) gave the spectrum of the excited state cross section shown in Fig. 3. The peak at 760 nm (1.63 eV) indicates a resonance in the excited state absorption.<sup>4,5</sup> The peak cross section,  $\sigma \approx 1.9 \times 10^{-17} \text{ cm}^2$ , is in order of magnitude agreement with values obtained from the picosecond photoinduced absorption<sup>4,5</sup> (the Z scan would generate an average over times less than the 8 ns pulse width) and much larger than the linear absorption cross section as required for reverse saturable absorption.<sup>13</sup> The spectrum of the picosecond PIA is shown for comparison as the solid curve in Fig. 3. The general agreement between the magnitude and spectral dependence of  $\sigma$  as obtained indirectly from the Z-scan data [using Eqs. (1) and (2)] and as obtained directly from the PIA confirms the proposed mechanism.

Utilizing this large nonlinear absorption, optical limiting was demonstrated; for 30  $\mu\text{m}$  films, there is both a large excited state absorption cross section and a reasonable linear transmission (44%) at 760 nm. The composite film was brought to the focus found from Z-scan measurements, and the input pulse energy was varied by rotating a polarizer between two fixed polarizers. The data are plotted in Fig. 4. The limiting function of the P3OT/[6,6]PCBCR blend is clearly established; at 5  $\mu\text{J/pulse}$  (0.3  $\text{J/cm}^2$  average fluence) the transmission is reduced to half of the linear transmission. Saturation occurs at  $E_{\text{out}} < 2 \mu\text{J/pulse}$  ( $\approx 0.1 \text{ J/cm}^2$ ) for higher inputs.

The measured  $E_{\text{out}}$  is somewhat greater than that predicted using Eqs. (1) and (2) (solid curve in Fig. 4) due to the weak intensity dependence of  $\beta_{\text{eff}}$ . The origin of such an intensity dependence can be a higher order negative nonlinearity, possibly nonlinear bleaching due to the thermochromic effect in P3OT.<sup>14</sup> The damage threshold was around 15  $\mu\text{J/pulse}$  ( $\sim 1 \text{ J/cm}^2$  in average fluence), above which there is a permanent change in the linear transmission.

Although materials containing  $\text{C}_{60}$  have been demonstrated as optical limiters, most were in the form of solutions.<sup>15–22</sup> Comparable optical limiting was reported for thick layers (each several millimeters thick) of  $\text{C}_{60}$  in polymethyl methacrylate when pumped on resonance at 532 nm.<sup>23</sup>

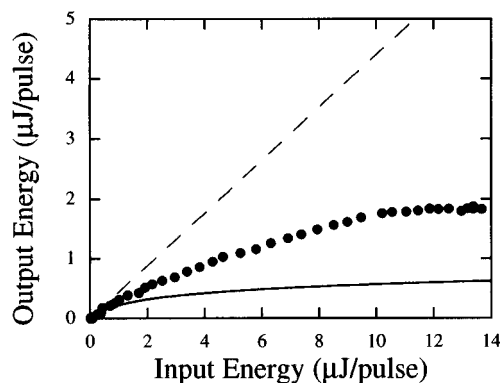


FIG. 4. Performance of an optical limiter made of the charge transfer film at 760 nm. Closed circles: experimental data; Dashed line: linear transmission line (44%); Solid curve: calculated response using the excited cross section obtained from the Z-scan experiment at low input energy levels.

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